No well-defined remnant Fermi surface in $Sr_2CuO_2Cl_2$

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In angle-resolved photoelectron spectra of the antiferromagnetic insulators $Ca_2CuO_2Cl_2$ and $Sr_2CuO_2Cl_2$ a sharp drop of the spectral intensity of the lowest-lying band is observed along a line in **k** space equivalent to the Fermi surface of the optimally doped high-temperature superconductors. This was interpreted as a signature of the existence of a remnant Fermi surface in the insulating phase of the high-temperature superconductors. In this paper it is shown that the drop of the spectral intensity is not related to the spectral function but is a consequence of the electron-photon matrix element.

It is of interest to understand the changes the normal-state electronic structure of the high-temperature superconductors (HTSCs) undergoes when doped from an antiferromagnetic insulator to a metal. Angle-resolved photoelectron spectroscopy (ARPES) has played an important role in the study of the electronic structure of the HTSCs in the different regions of the doping phase diagram. Recently ARPES experiments using $Sr_2CuO_2Cl_2$ and $Ca_2CuO_2Cl_2$ single crystals yielded information on the electronic structure of the HTSCs in the limit of very low hole doping. [1–4]

$Sr_2CuO_2Cl_2$ and $Ca_2CuO_2Cl_2$ are closely related to the undoped parent compounds of the HTSCs, as they are also antiferromagnetic insulators with Néel temperatures of 255 and 247 K, respectively. [5,6] The CuO_2 planes in $Sr_2CuO_2Cl_2$ and $Ca_2CuO_2Cl_2$ are undoped (half-filled); therefore the spectral intensity in an electron energy-distribution curve (EDC) related to the CuO_2 plane gives information about the dynamics of a single hole (the hole created by photoionization) in a CuO_2 plane. Of primary interest are the lowest-lying states in an ARPES spectrum, the so-called first electron-removal states. In $Sr_2CuO_2Cl_2$ and $Ca_2CuO_2Cl_2$ these show a well-developed low-binding-energy peak only for **k** vectors in the vicinity of $(\pi/2,\pi/2)$ where the peak has its minimum binding energy. [1–4,7] The low-binding-energy peak is followed by additional spectral weight at higher binding energies. Outside this **k** space region the first feature is a rather broad structure with its maximum located at higher binding energy.

In the published $Sr_2CuO_2Cl_2$ and $Ca_2CuO_2Cl_2$ ARPES data the spectral intensity of the first electron-removal states shows a sudden drop along a line in **k** space which closely resembles the Fermi surfaces found in band-structure calculations or ARPES data of optimally or overdoped HTSCs. [4] Insulators such as $Sr_2CuO_2Cl_2$, $Ca_2CuO_2Cl_2$ and the undoped parent compounds of the HTSCs do not have partially filled bands and hence no Fermi surface, but it was argued that there exists a remnant of the Fermi surface of their respective metallic phases in the sense that when the first electron-removal states of $Sr_2CuO_2Cl_2$ or $Ca_2CuO_2Cl_2$ cross this remnant Fermi surface, their spectral intensity suddenly drops, in analogy to the behavior of the ARPES spectral intensity related to the lowest-lying band of a metal when it crosses the Fermi surface. Comparing the binding energies of the first electron-removal states of the copper oxychlorides for **k** vectors on the remnant Fermi surface one can formally define a gap, zero for **k** on the remnant Fermi surface where the low-binding-energy peak has minimum binding energy, and maximum for **k** on the remnant Fermi surface where the low-binding-energy peak has maximum binding energy. It was noted that the gap defined this way shows an analogous **k** dependence as the superconducting gap of the HTSCs, i.e. a d-wave-like dispersion. [4] This d-wave-like behavior of the first electron-removal states of the copper oxychlorides would naturally explain the **k** dependence of the normal-state gap encountered in the underdoped HTSCs: upon hole-doping the chemical potential drops to the maximum of the d-wave-like dispersion (the node of the "gap") of the insulator. In the underdoped regime the Fermi level only touches states near the node of the d-wave-like gap of the insulator, forming small segments of the Fermi surface, while the portions of the remnant Fermi surface around $(\pi,0)$ remain gapped.

However, in ARPES, the spectral intensity of an EDC is directly proportional to the electron-photon matrix-element weighted spectral function [8] and not the spectral function itself. Calculations suggest that the relationship between ARPES intensities and the underlying electronic structure can be complicated due to matrix element effects and that caution should be exercised in interpreting detailed features of the ARPES intensities in terms of the spectral function. [9] In a recent paper, using ARPES of $Sr_2CuO_2Cl_2$ as an example, it was demonstrated experimentally that for layered cuprates

the electron-photon matrix element can have a significant impact on both the relative spectral intensity and the shape of a feature in an ARPES spectrum. [10] In this paper ARPES measurements on a $Sr_2CuO_2Cl_2$ single crystal along the line Γ to (π,π) in $\mathbf{k}$ space, using different photon energies in the range from 20 to 24 eV, are presented. It will be shown that the sudden drop in spectral intensity observed in the ARPES spectra of $Sr_2CuO_2Cl_2$ along a line in $\mathbf{k}$ space similar to the Fermi surface of HTSCs is not due to a similar drop in the spectral function due to a remnant Fermi surface but is caused by the electron-photon matrix element i.e. is not a feature of the electronic structure of these compounds but an artifact of the photoexcitation.

The ARPES were recorded on the Ames Laboratory/Montana State University ERG/SEYA beamline at the Synchrotron Radiation Center, using a 50 mm radius hemispherical analyzer with a $2°$ full angular acceptance angle, corresponding to a $\mathbf{k}$ resolution of 0.034 Å^{-1} and 0.038 Å^{-1} (6 % and 6.8 % of the distance between Γ and (π,π)) for the first electron-removal states and 20 eV and 24 eV photon energy, respectively. The total energy resolution was 105 meV. The angle of incidence of the photons was $\sim43°$ with respect to the sample surface normal with the sample normal pointing down by $\sim8°$. The $Sr_2CuO_2Cl_2$ single crystal was grown as described elsewhere [11]. The sample was oriented *ex situ* by Laue backscattering and mounted with the Cu-O bonds in a horizontal/vertical plane. The sample was cleaved (cleavage plane parallel to CuO_2 planes) in the experimental chamber in a vacuum better than 4×10^{-11} Torr and sample alignment was confirmed *in situ* by using the symmetry of the dispersion of spectral features at high-symmetry points and the appearance of acute peaks associated with purely O $2p$-derived states in the main valence band at ~2.5 and ~4 eV at (π,π) and $(\pi,0)$, respectively. [12] All EDCs were recorded at room temperature and were normalized to the photon flux. Although there is no long-range antiferromagnetic order at room temperature in $Sr_2CuO_2Cl_2$, the antiferromagnetic correlation length is still two orders of magnitude larger than the Cu-O distance [5]. Therefore photoemission, as a fast and local probe, still sees the effect of antiferromagnetic order, even 50 K above the Néel temperature [1]. The Fermi edge of a Pt foil in electrical contact with the sample was used as binding-energy reference. There were no indications of charging effects because repeating an EDC after the beam had decayed to less than half the current when the first EDC was taken gave the same EDC, when normalized to the incident flux. All spectra shown were recorded within a period of five days after the cleave of the sample and in one experimental run, i.e., using the same sample cleave. We observed no signs of sample degradation during this span of time.

Figure 1 presents the first electron-removal states of $Sr_2CuO_2Cl_2$ for $\mathbf{k}$ along Γ - (π,π) for photon energies from 20 to 24 eV. For all photon energies a dispersing low-binding-energy peak is observed which has its minimum binding energy at $(\pi/2,\pi/2)$. There is a significant change in the spectral intensity of the low-binding-energy peak as a function of $\mathbf{k}$ for different photon energies. For 24 eV, the low-binding-energy peak has non-negligible spectral intensity for $\mathbf{k}$ from 38 to 51 % of the distance between Γ and (π,π). Upon lowering the photon energy, the center of the $\mathbf{k}$ span in which this peak exists along the line Γ to (π,π) shifts to bigger $|\mathbf{k}|$. For example, for 22 eV photons the low-binding-energy peak can be observed for $\mathbf{k}$ from 39 to 58 % of the distance between Γ and (π,π), while for 20 eV photon energy, it has significant spectral intensity from 49 to 60 % of the distance between Γ and (π,π). This trend is exemplified in Fig. 2, which shows the integrated spectral intensity of the low-binding-energy peak associated with the momentum density $n(\mathbf{k})$. It is evident that the maximum of $n(\mathbf{k})$ shifts from ~40 to 55 % of the distance between Γ and (π,π) on going from 24 to 20 eV photon energy. This is a substantial shift, given the fact that along Γ - (π,π) in $\mathbf{k}$ space there is only a low-binding-energy peak from ~33 to ~60 % of the distance between Γ and (π,π).

Note that the observed differences between the series of EDCs shown in Fig. 1 can only be related to the electron-photon matrix element. Sample variability can be excluded as the spectra were recorded using the same sample and cleave. Furthermore, our data are compatible with previously published $Sr_2CuO_2Cl_2$ and $Ca_2CuO_2Cl_2$ ARPES results (if recorded at the same photon energy) which eliminates a bad sample cleave or misalignment of the crystal as possible reasons. One could argue that, dependent on photon energy, different initial states are observed, but this is not consistent with the continous shift of spectral intensity of the low-binding-energy peak to bigger $\mathbf{k}$ vectors evident in Fig. 1 when the photon energy is decreased. Moreover, up to now most authors ascribe the low-binding-energy peak evident in the first electron-removal states of $Sr_2CuO_2Cl_2$ or $Ca_2CuO_2Cl_2$ to a Zhang-Rice singlet (ZRS) [13,14], i.e. one initial state. For an initial state with a given $\mathbf{k}$ component parallel to the CuO_2 planes the momentum component perpendicular to the CuO_2 planes is dependent on the photon energy but a ZRS is localized in a CuO_2 plane; therefore no dependence of the dispersion of the low-binding-energy peak on the momentum component perpendicular to the CuO_2 plane is expected. Note also that the in-plane nature of the counterpart of the first electron-removal states in the unoccupied part of the electronic structure (which is derived from the same orbitals as the first electron-removal states) has been explicitly shown by x-ray absorption spectroscopy. [15] The spectral function itself does not depend on the photon energy used to excite the first electron-removal states. The Γ - (π,π) series of spectra shown in Fig. 1 are equivalent in the sense that they show the lowest-lying excitations associ-

ated with the motion of a hole in an antiferromagnetically ordered CuO_2 plane for **k** along the Γ- (π,π) line in the first Bz, i.e. the underlying spectral function is the same. The electron-photon matrix element $\langle$ i $|$ **p·A** $|$ f $\rangle$ (**p** and **A** are the photoelectron momentum and the vector potential, respectively), on the other hand, is affected by the photon energy as different final states are reached upon changing the photon energy. It therefore is the factor which is responsible for the observed differences between the series of EDC's shown in Fig. 1.

From the preceeding discussion we can conclude that the spectra shown in Fig. 1 truly represent the low-binding energy ARPES response of $Sr_2CuO_2Cl_2$ for 20 to 24 eV photon energy and **k** from Γ to (π,π) and it has become clear that the spectra are significantly influenced by the electron-photon matrix element. These data show that the lowest-lying band does not cross a sharp remnant of a Fermi surface. Firstly, note that in this kind of scenario the lowest-lying band would disperse to lower binding energies on going from Γ to $(\pi/2,\pi/2)$ and cross the remnant Fermi surface before it disperses back to higher binding energies again i.e. for **k** before $(\pi/2,\pi/2)$. This implies that in Fig. 1 the peak associated with the lowest-lying band should lose most of its spectral intensity before $(\pi/2,\pi/2)$. This is the case for 24 and 23 but not for 20 and 21 eV photon energy where this peak has most of its spectral intensity for **k** between $(\pi/2,\pi/2)$ and (π,π). According to Ref. [4], a way to locate the crossing of the Fermi surface (or remnant Fermi surface) is to determine the **k** for which n(**k**) of the low-binding-energy peak as a function of **k** has its steepest descent. Applying this method on our $Sr_2CuO_2Cl_2$ ARPES data, it is clear that due to the influence of the electron-photon matrix element we do not get a result which is robust for 20 to 24 eV photon energy as the **k** where there is the steepest descent in n(**k**) from the low-binding-energy peak along Γ to (π,π) (Fig. 2) varies from ~50 to ~63 % of the distance between Γ to (π,π) for 24 to 20 eV photon energy, which, as already noted, is a substantial shift compared with the **k** space range where there exists a low-binding-energy peak in the first electron-removal states of $Sr_2CuO_2Cl_2$.

The fact that there is a distinct low-binding-energy peak for **k** on a line from $(\pi/2,\pi/2)$ to (π,π) and that the steepest descent of the integrated spectral intensity of the low-binding-energy peak along Γ to (π,π) is not found at the same **k** for different photon energies represents evidence against the existence of a well-defined remnant Fermi surface for $Sr_2CuO_2Cl_2$. Nonetheless, the existence of a remnant Fermi surface for $Sr_2CuO_2Cl_2$ cannot be ruled out unless it is also proven that the intensity of the low-binding-energy peak for **k** along Γ - $(\pi/2,\pi/2)$ is not much bigger than for **k** along $(\pi/2,\pi/2)$ - (π,π). Note that this possibility still exists, as the low-binding-energy peak is best developed for **k** along Γ - $(\pi/2,\pi/2)$ for a different photon energy (23 eV) than for **k** along

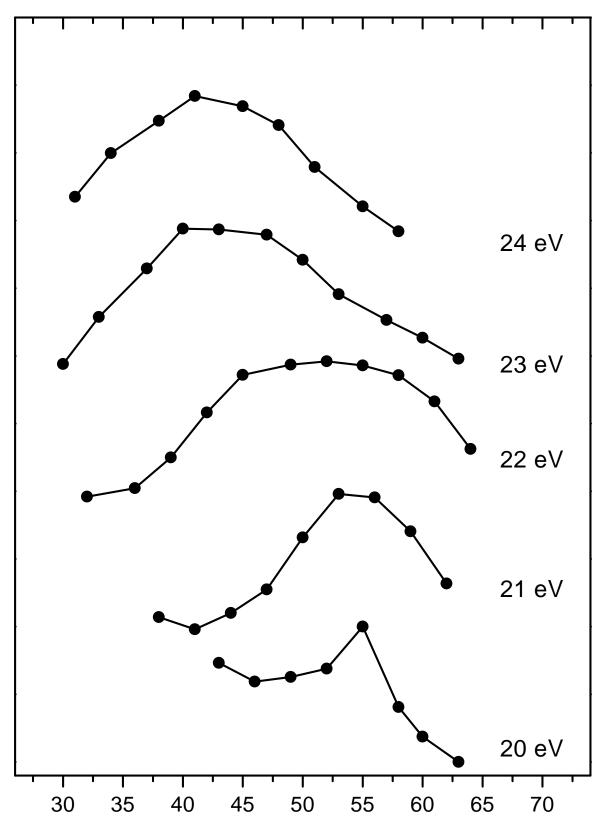$(\pi/2,\pi/2)$ to (π,π) (21 eV). This means that it still could be possible that the intensity of the low-binding-energy peak in the spectral function is quite different for **k** along Γ - $(\pi/2,\pi/2)$ and along $(\pi/2,\pi/2)$ - (π,π). It is clear that a much bigger intensity of the low-binding-energy peak for **k** along Γ - $(\pi/2,\pi/2)$ than for **k** along $(\pi/2,\pi/2)$ - (π,π) would be compatible with a sharp decrease of the integrated intensity of this peak on going from Γ to (π,π) and a remnant Fermi surface. In Fig. 3 the first-electron removal states of $Sr_2CuO_2Cl_2$ are shown for **k** vectors at 44 and 56 % of the distance between Γ and (π,π) [i.e. equidistant to $(\pi/2,\pi/2)$] for photon energies from 20 to 24 eV. If there exists a remnant Fermi surface in $Sr_2CuO_2Cl_2$ it is expected that the spectral intensity of the peak at 56 % of the distance between Γ and (π,π) and for the photon energy where it is best developed (21 eV) is much smaller than the maximum peak intensity one can get at 44 % of the distance between Γ and (π,π) (at 23 eV photon energy) which evidently is not the case. In conjunction with the results presented in the preceeding paragraph this is clear evidence that in the case of $Sr_2CuO_2Cl_2$ the lowest-lying band does not cross a remnant Fermi surface on going from Γ to (π,π).

In conclusion the spectral function associated with the motion of a hole in an antiferromagnetically ordered background has been probed by ARPES of the antiferromagnetic insulator $Sr_2CuO_2Cl_2$. Along the line Γ to (π,π) in **k** space we have observed that the strong drop of the spectral intensity of the lowest-lying states reported in the literature is not related to a crossing of the lowest-lying band of a remnant Fermi surface but is due to the electron-photon matrix element.

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FIG. 1. The first electron-removal states of $Sr_2CuO_2Cl_2$ recorded along the Γ to (π,π) direction of the first BZ using 20 to 24 eV photon energy. The **k** vectors are given in % of the distance between Γ and (π,π).

FIG. 2. Integrated spectral intensity of the low-binding-energy peak of the first electron-removal states of $Sr_2CuO_2Cl_2$ deduced from the spectra shown in Fig. 1. **k** vectors are given in % of the distance between Γ and (π,π).

FIG. 3. Comparison of the first electron-removal states of $Sr_2CuO_2Cl_2$ recorded at 44 (open circles) and 56 % (solid circles) of the distance between Γ and (π,π) for 20 to 24 eV photon energy. The spectra are offset vertically for clarity but are on-scale otherwise.